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DETROIT

Ceramics for Piezoelectric Transducers

lead-compound systems show promise

THE NATIONAL BUREAU OF STANDARDS has developed several lead oxide based piezoelectric ceramics that have excellent electromechanical properties and are stable over a wide temperature range. Some of these compositions, particularly in the lead titanate-lead zirconate system and the lead titanate-lead zirconate-lead oxide: tin oxide system, are expected to find considerable application as transducers. They may furnish sensing elements in accelerometers, sound detectors, sonar, velocimeters, strain and pressure gages, and as drivers in ultrasonic devices. These materials can be expected to replace barium titanate in many commercial applications and to extend the use of ceramic transducers. The compositions were developed under the sponsorship of the Army's Office of Ordnance Research by Bernard Jaffe, R. S. Roth, and Samuel Marzullo of the mineral products laboratories.

Piezoelectric ceramics are widely used as transducers for energy conversion between electrical signals and mechanical motion. Barium titanate has been used for many transducer applications, but these applications have been seriously limited because of its narrow temperature range—from 20° to 100° C. To overcome this limitation, and to improve the properties of ceramic transducers, the Bureau developed lead oxide based ceramics of particular compositional ranges having a response that is uniform over a much wider temperature interval.

The lead oxide based compositions have better electromechanical properties than the previously developed barium titanate ceramics because the proportions of their ingredients place them close to the boundary where morphotropic transformation—an abrupt change in the solid-solution phase—takes place. The Bureau discovered that when the solid-solution phases of certain lead oxide compositions are ferroelectric on both sides of the morphotropic boundary, the material yields ceramic transducers that have more desirable properties over a wider range of temperature than other compositions of similar crystalline structure.

Studies indicate that piezoelectric ceramics can be made only from ferroelectric crystalline materials. Barium titanate is an example of such a material. Its properties are enhanced at temperatures near those of polymorphic transformations below the Curie temperature. This effect is observed near 0° C., where the crystal form changes from one ferroelectric modification of the perovskite structure to another. Compositional boundaries (morphotropic transformations) have been observed between ferroelectric phases of slightly differing structure. One example of morphotropism between ferroelectric phases in solid solution is found in the lead zirconate-lead titanate system. Experi-ments at NBS on this system [1] show that the room-temperature dielectric constant and the induced piezoelectric effects are enhanced as the composition ap-

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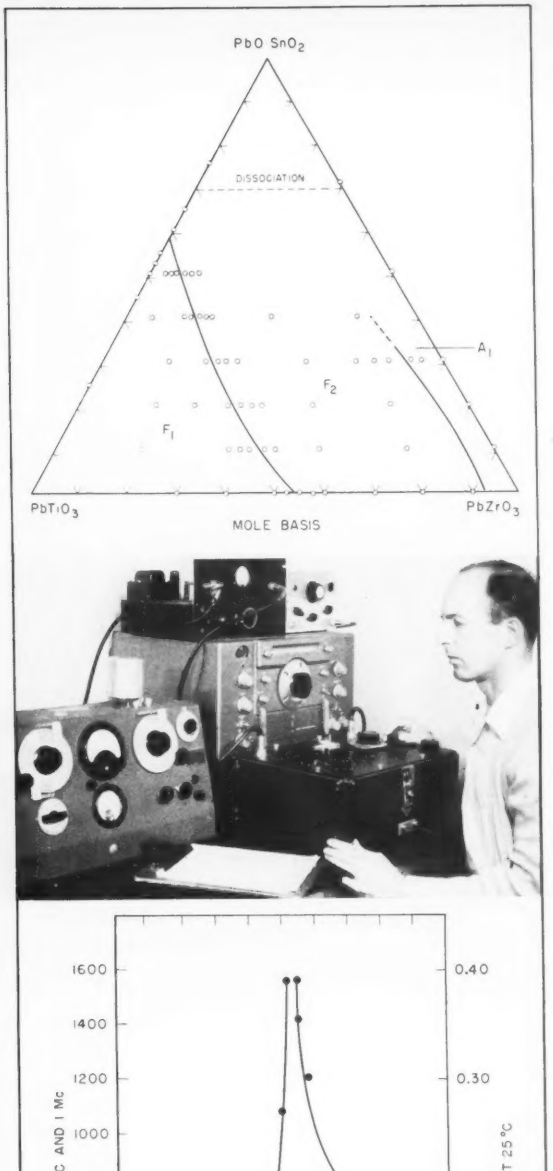


proaches the phase boundary. For best piezoelectric and dielectric properties, the results indicate that compositional proximity to a morphotropic transformation appears to be more desirable than temperature proximity to a polymorphic transformation. As a consequence of these indications, experiments were continued on such solid-solution systems where morphotropic transformations can be found.

In the experiments on the new compositions, X-ray diffraction analyses were performed on matured ceramic specimens to determine the symmetry of the phases present in the solid solutions. The diffraction analyses were followed by measurement of the dielectric and piezoelectric properties. Among the compositions investigated were the lead titanate-lead zirconate, lead titanate-lead oxide : tin oxide, lead zirconate-lead oxide : tin oxide, and the lead titanate-lead hafnate binary systems; and the ternary systems, lead titanate-lead zirconate-lead oxide : tin oxide.[2] Although the mixture lead-oxide : tin oxide is not a compound, single-phase solid solutions can be formed with this material in combination with lead-titanate or lead-zirconate. Many variations in the proportions of the ingredients in these systems were examined. Morphotropic boundaries were found in a number of the systems. The dielectric and piezoelectric properties of all the compositions close to the morphotropic boundary were greatly enhanced.

One of the most useful compositions found in this investigation is that containing 45 percent of lead-titanate, 55 percent of lead-zirconate.[3] Its Curie point is approximately 340°C, compared with a Curie temperature of 120°C for barium-titanate. The far higher Curie point of this new mixture greatly extends the useful temperature range of ceramic transducers. The lead titanate-lead zirconate has a radial coupling coefficient of greater than 0.3 at 275°C, and a piezoelectric voltage output coefficient (g_{31}) of 11.7×10^{-3} voltmeter per newton. The voltage coefficient is more than twice that of commercial barium-titanate, while the piezo-

The Bureau has developed several lead-oxide based piezoelectric ceramics that have excellent electromechanical properties and are stable over a wide temperature range. *Top:* Phase diagram for the ternary system $PbTiO_3$-$PbZrO_3$-PbO: SnO_2. A morphotropic phase boundary separates ferroelectric tetragonal solid solutions (F_1) from ferroelectric rhombohedral solid solutions (F_2). Dielectric and piezoelectric properties are enhanced along this morphotropic boundary. A second boundary separates ferroelectric rhombohedral solid solutions from the antiferroelectric solid solutions (A_1). Dissociation occurs in high PbO: SnO_2 portion of the system. *Middle:* Operator is measuring the dielectric constant of a transducer. These new compositions can be expected to replace the barium titanate ceramics for applications in accelerometers, sound detectors, pressure gages, and other devices. *Bottom:* Graph of dielectric constant (ϵ) at 1 Mc and radial coupling coefficient (k_r) for ceramic compositions studied in system $PbTiO_3$-$PbZrO_3$. Solid solutions on $PbTiO_3$ side of morphotropic boundary—at 45 percent $PbTiO_3$—are tetragonal, while those on $PbZrO_3$ side are rhombohedral. Dielectric and piezoelectric properties of compositions near morphotropic boundary are greatly superior to other compositions in the system.

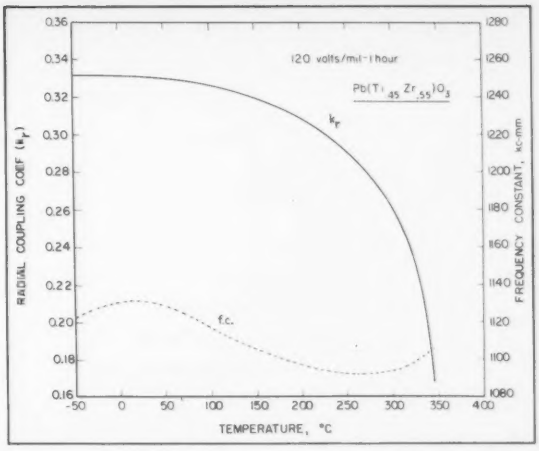
electric charge output coefficient (d_{31}) of both materials are comparable. Because of the high voltage coefficient, this lead titanate-lead zirconate ceramic is particularly adaptable as a sensing element to convert mechanical motion or force to an electrical signal.

The addition of lead oxide: tin oxide to the lead titanate-lead zirconate provides another useful composition in the form 47¼ percent of lead-titanate, 22¾ percent of lead-zirconate, 30 percent of lead oxide: tin oxide. This composition has the highest piezoelectric charge output coefficient (d_{31}) of all the compositions examined—74×10^{-12} coulomb per newton. The high charge coefficient makes this material useful as a driver or generator of mechanical motion.

[1] Piezoelectric properties of lead zirconate-lead titanate solid-solution ceramics, *B. Jaffe, R. S. Roth, and S. Marzullo, Jr., Appl. Phys.* **25**, *6, 809 (1954)*.

[2] Properties of piezoelectric ceramics in the solid-solution series lead titanate-lead zirconate-lead oxide: tin oxide and lead titanate-lead hafnate, *B. Jaffe, R. S. Roth, and S. Marzullo, J. Research NBS (in press)*.

[3] *U. S. Patent No. 2,708,244 (May 10, 1955), B. Jaffe,* Piezoelectric transducers using lead titanate and lead zirconate, *Filed March 24, 1954.*



Graph showing radial coupling coefficient (k_r) and frequency constant (f. c.) versus temperature for the composition $Pb(Ti_{.45}Zr_{.55})O_3$. Properties shown are those of typical specimen which had been previously polarized at 120 v/mil for 1 hr. This composition gives good piezoelectric response at intermittent usage up to 275° C.

Test for Instrument Cable Noise

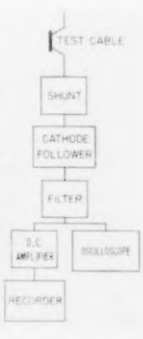
THE BUREAU has developed a method of obtaining an objective, reproducible "noise index" for instrument cables subjected to shock, vibration, or transient pressures. This rapid, sensitive test provides a readily interpreted index for cables of varied size, construction, and rigidity. Such data should prove of value to cable manufacturers, specification writers, manufacturers, and users of instrument equipment. The technique was devised by T. A. Perls [1] under a program of basic instrumentation sponsored at the Bureau by the Department of Defense and the Atomic Energy Commission.

Whenever an instrument cable is used where it is subjected to mechanical forces, a special problem exists for the scientist or engineer making the measurements. Strains induced in the cable by such forces produce spurious voltages (noise) that interfere with the measurement of the desired signal. Cable noise is a problem in such fields as air and underwater explosion studies and shock and vibration research. These spurious voltages also interfere with the proper performance of such devices as hearing aids, phonograph pickups, and crystal-type microphones.

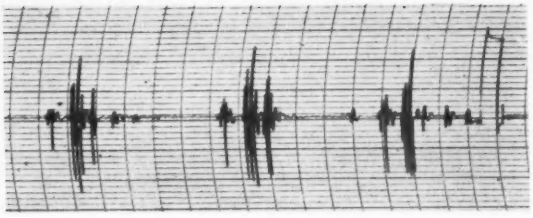
Recent theoretical work [2] has shown that noise signals are due to currents set up in the cable when a temporary separation occurs between a small portion of the dielectric and either conductor. Some of these currents flow through the terminal impedance of the cable and ultimately appear on the other conductor at a point opposite the separated charge on the dielectric. To free the cable of these noise signals, it is only necessary that both surfaces of the dielectric be covered by a well-bonded conductive coating.[3]

Partially as a result of this work, there has been a renewal of interest in low-noise cables. Recently, several U. S. manufacturers began producing a Bureau-developed cable under a nonexclusive, royalty-free Government license.[4] Other low-noise cables have become available, some as early as 1943 in Great Britain.

With the appearance of these various cables, questions arose as to the relative merits of each. It became apparent that an objective, readily reproducible test was needed, so that a meaningful noise index could



In the test method for measuring the "noise index" of instrument cables, a weighted cable is dropped from a horizontal position and allowed to swing freely between two clamps. The cable's generated noise is read as the maximum peak-to-peak electrical output. Noise recording apparatus is on bench. *Insert:* Schematic diagram of equipment.



Sample record obtained in test for cable noise. Three groups of oscillations correspond to three successive sets of swings. Recorder speed is one division per second. Rectangular step (right) represents 72 mv at the preamplifier input.

be arrived at for each cable. The NBS test is designed to provide such an index without the use of a complicated procedure or unusual equipment.

The mechanical treatment used in the test is adapted from a recently devised Bureau of Ships technique for determining low-noise cable characteristics.[5] In the NBS test, a 7-ft length of cable is fitted with a connector at one end and left electrically open, but shielded, at the other end. A 5-ft section of this cable is suspended between two points 4 ft apart and a weight is clamped at the section's midspan. To eliminate dependence on cable size, the attached weight is made approximately equal to the mass of 40 ft of the test cable. The cable is connected to two amplifiers in series which have a reasonably flat frequency response from 5 to 40 cps. In the setup the noise output is read on a recorder.

The center of the cable, with weight attached, is moved upward through an arc until the cable is lying in a horizontal plane. When the cable and weight are released from this position, and allowed to swing freely, noise is generated in the cable. The noise is recorded as a series of sharp voltage peaks of varying heights, both positive and negative in sign. The noise index is the sum (without regard to sign) of the maximum positive and negative. In the setup, this index is the number of picocoulombs (a picocoulomb is 10^{-12} coulomb) generated with a total capacitance of 1,000 picofarads, into a 10-megohm load. This also turns out to be the number of millivolts recorded under these conditions. The noise figure for any particular sample is repeatable within ± 30 percent, but may vary by a factor of 3 or more for different samples of the same cable.

The maximum noise voltage in any particular test will be attained only if the separation of charge in the cable takes place in a time which is short compared to the time constant of the circuit. The time constant, RC, is determined by the input resistance R to the first amplifier and the total capacitance C of the cable and any shunts used. In practice, this means that if the time constant is made large compared to charge-separation time, then the charge transferred in any particular test should be nearly independent of both the total capacitance and the input impedance of the amplifier. Thus, if the noise test produces separations which take place more slowly than under the actual conditions of use, the circuit's time constant must be adjusted to accommodate these relatively slow separations. If this adjustment is made, the charge observed in the test may then be taken as a noise index applicable to many conditions of cable use. For the NBS system, it was found that the critical time constant above which the generated charge becomes nearly independent of the time constant is about 0.01 sec.

Since the recorded voltage is inversely proportional to the total capacitance, the total capacitance should be chosen as small as practicable. For example, with a 10-megohm input resistance to the preamplifier, the required time constant of 0.01 sec is obtained with a total capacitance of 1,000 picofarads. With the capacitance of commercial cables ranging up to approximately 100 picofarads per foot, the total capacitance of the required 7-ft length of cable is well within this figure.

The frequency spectrum of the noise generated is determined in the following manner. A test cable, shunted with sufficient capacitance to make the total equal to 1,000 picofarads, is connected through a cathode follower and a variable band-pass filter to a d-c amplifier and recorder. The filter is set so that its half-power points are two octaves apart. Beyond these points the power drops off at the rate of approximately 24 db per octave. Observations indicate that the generated noise has appreciable frequency components at both the frequency of the cable swing (approximately 0.7 cps) and at twice that frequency. In addition, another broad maximum is found in the range between 4 and 40 cps. This latter range was chosen for the tests to best simulate the actual conditions of cable use. Also, use of this range made it possible to discriminate against radiofrequency interference at the lower frequencies.

It was found experimentally that under controlled conditions of impedance, time constant, and frequency response, the particular mechanical treatment given the cable is unimportant. Thus, the noise recorded with a sufficiently large time constant varies only by a factor of 5 at most when any one cable is subjected successively to whipping, twisting, slapping, hitting with a hammer, and swinging. The noise generated by different cables on the other hand, varies by as much as a factor of 10,000. It appears then that if impedance, time constant, and frequency-response conditions are known, other tests may be interpreted to yield values comparable to those of the NBS test.

[1] *Now at the Missile Systems Division, Lockheed Aircraft Corp., Van Nuys, California.*

[2] Electrical noise from instrument cables subjected to shock and vibration, *by T. A. Perls, J. Appl. Phys.*, **23**, *674 (June 1952).*

[3] Noise-free instrument cable, *NBS Tech. News Bull.* **36**, *37 (March 1952).*

[4] *U. S. Patent No. 2,690,469 of September 28, 1954, to T. A. Perls, assigned to the U. S. Government. Foreign patents have also been issued as follows: Canada, No. 495,648 (September 1953); France, No. 1,069,286 (February 10, 1954); United Kingdom, No. 716,540 (January 10, 1955).*

[5] Coaxial cable noise test, *by J. Hannon, Memorandum, Ser. 817A3-M-1561A, Bureau of Ships, Dept. of the Navy, Washington 25, D. C. (August 21, 1953).*

Rapid Analysis of Vulcanizates

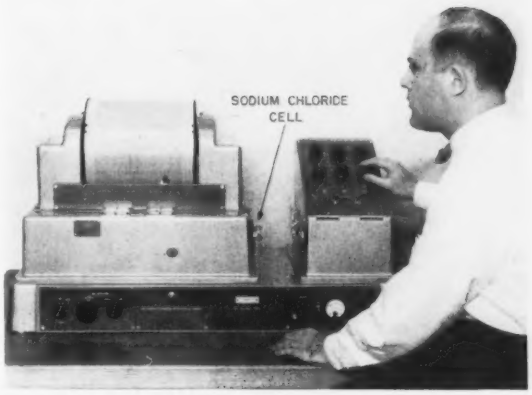
THE BUREAU has developed a rapid, convenient method for determining natural rubber in vulcanizates of GR–S [1] and natural rubber. Based on studies [2] by M. Tryon, E. Horowitz, and J. Mandel of the NBS staff, the procedure involves thermal decomposition of the vulcanizates and infrared spectroscopic analysis of the resulting products. This method will make it possible to perform quantitative analyses of polymeric materials that have defied analysis because of their insoluble nature or the presence of interfering fillers.

Until now methods for quantitative estimation of natural rubber in vulcanized samples have been difficult and time consuming. The direct analytical method involves successive steps where the sample is extracted, dried, and digested by chromic acid. A distillate of acetic acid, formed during oxidation of the sample, is titrated; and calculation of rubber hydrocarbon content is based on the yield of acetic acid. The direct method, besides being involved, often gives erroneous results for mixtures of natural and synthetic rubber. The indirect method is even less satisfactory. Here, all the nonrubber hydrocarbon constituents are determined, and the rubber content calculated by difference. The limitations of this method, especially in determining the nonrubber constituents, make the results subject to large cumulative errors; and no differentiation between natural and synthetic rubber is possible.

In the NBS method, the sample is milled and extracted with acetone, and the solvent removed by vacuum drying. A 0.5-g specimen is pyrolyzed in a modified combustion furnace at 550°C. One or two drops of the liquid distillate are placed between two sodium chloride windows having a lead spacer 0.025 mm thick. Each liquid distillate obtained upon pyrolysis is analyzed with a recording spectrophotometer using sodium chloride optics. The concentration of natural rubber is determined by comparing the relative intensity of absorption bands at wavelengths characteristic of natural rubber and GR–S. These bands are 11.25 microns for natural rubber and 11.02 microns for GR–S. The pyrolysis of the sample and its infrared analysis require about 15 min, compared to 4 hr or more for analysis by the usual direct or indirect methods.

In the course of his analysis, the operator uses a calibrating curve relating the ratio of transmittances of GR–S and natural rubber to the concentration of natural rubber. The work has established that the log of this ratio is nearly a linear function with respect to the concentration of natural rubber, based on the total polymer weight.

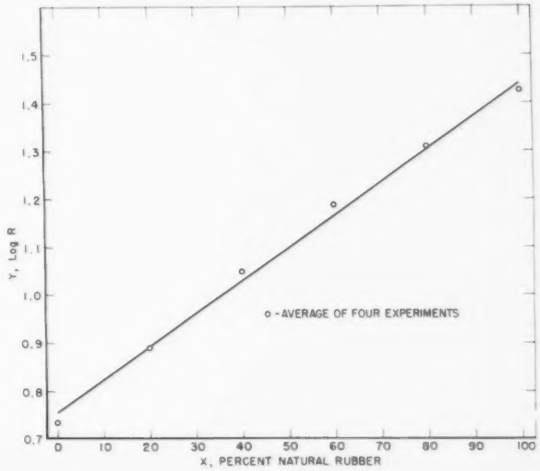
This method should also be of value in more fundamental studies of polymer degradation and depolymerization. Here it could be used to obtain additional data on pyrolysis products unsuited to mass spectrometry.



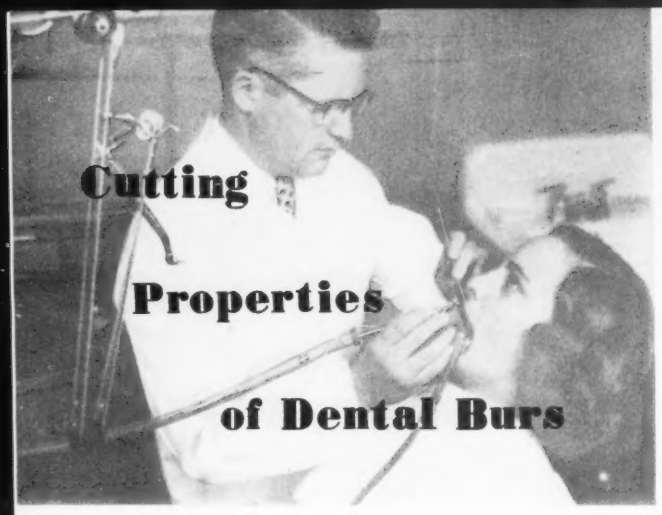
Analyzing distillates of rubber vulcanizates on recording spectrophotometer. Drops of distillate are placed between sodium chloride windows and mounted between light source and analyzing-recording mechanism. Controls for wavelength and slit width are shown at left. The operator is controlling the scanning rate.

[1] *GR–S is the synthetic rubber made by copolymerizing butadiene and styrene.*

[2] *For further technical details, see* Determination of natural rubber in GR–S natural rubber vulcanizates, *by M. Tryon, E. Horowitz, and J. Mandel, J. Research NBS,* **55**, *219 (1955) RP2623.*



Calibration curve relating percent of natural rubber to infrared transmittance. On *Y*-axis, $R=10\frac{T_{11.02}}{T_{11.25}}$ where *T* is transmittance obtained from measurements at wavelengths 11.02 and 11.25 microns, corrected for background. Precision of single determination is indicated by a standard deviation of 0.023, representing about 3 percent natural rubber.



Cutting Properties of Dental Burs

high-speed rotation decreases discomfort and increases efficiency

Research indicates that eccentricity of rotating dental burs causes vibration at frequencies distressing to patients. This information was obtained in a study [1] recently completed by Col. D. C. Hudson and Major J. L. Hartley, guest workers from the U. S. Air Force Dental Service, Pfc. Robert Moore of the U. S. Army, and W. T. Sweeney of the NBS dental research section. The investigators also found that: (1) high-speed rotations of true-running dental instruments produce vibrations above the frequencies causing greatest distress; and (2) burs and diamond wheels cut more effectively at higher speeds.

Until a few years ago, dentists knew little regarding the cutting action of dental burs on human teeth. Data on industrial cutters is not entirely applicable to dental instruments because the properties of tooth enamel and dentin differ from other materials and because dental instruments are so much smaller than industrial cutters. Besides, the problem is complicated by the subjective element introduced by the patient. The primary aim of the NBS work in this field has been to discover how the rotating dental instrument may be most effectively operated without injuring vital structures through high temperatures [2] or vibration and with minimum discomfort to the patient. A second aim has been to gather data for use by the armed services in specifying standards for procurement of rotating dental instruments.

Previous work in other laboratories has shown that vibrations applied to teeth in the frequency range between 100 and 300 cps produce the most unfavorable patient response.[3] Unfortunately, frequencies in the range 100 to 200 cps are dominant in eccentric burs rotated at 6,000 to 10,000 rpm—speeds now used by many practitioners. The NBS investigation attempted to find out what degrees of bur eccentricity at what speeds cause vibrations in the distressing range.

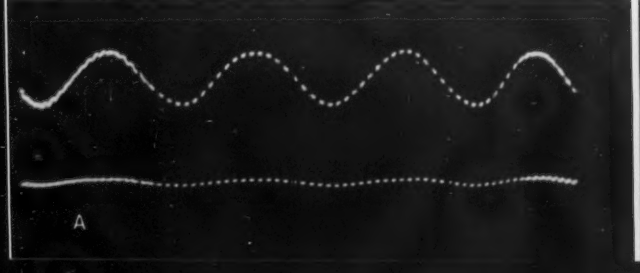
In order to do this, a number of steel and carbide burs and diamond abrasive wheels from various suppliers were studied. The abrasive wheel or bur under investigation was mounted and rotated in a draw collet chuck. A hard steel vane was held between the rotating instrument and a mutual-inductance transducer,[4] energized by a low-powered RF generator. The micrometer pickup reacted to minute movements of the vane as it was caused to shift by irregularities in the rotating instrument. Output of the vibration pickup was placed on an oscilloscope screen for photographing and study.

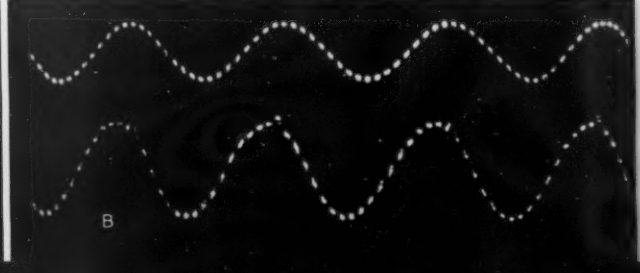
The rotating chuck was precision-machined so that any displacement of the steel vane was caused by the eccentricity or surface irregularity of the dental bur. The pickup was mounted on a small carriage that rolled on machined tracks. Weights, attached to cords hanging from the carriage, held the mutual-inductance transducer in proximity to the vibrating vane.

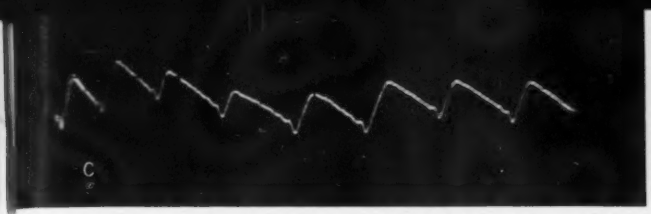
It was found that a true-running eight-bladed bur rotating at 10,000 rpm produced eight low-amplitude peaks per revolution at a frequency of 1,330 cps. However, a similar but eccentric bur rotating at the same speed produces a fundamental frequency of 166 cps with amplitude proportional to the amount of eccentricity.

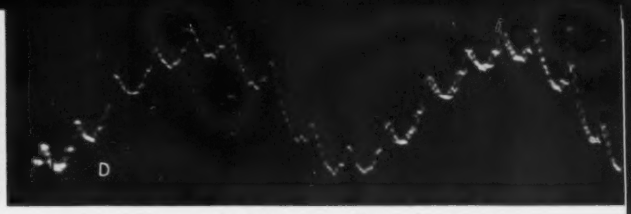
The data regarding vibration will be applied to clinical practice as rotating instruments are improved. If eccentricity of dental burs is kept small and symmetry of cutting heads increased, the chatter and vibration in the range of frequencies most annoying to patients can be reduced. However, even the most accurate bur will not perform properly in a handpiece that does not operate smoothly. Therefore, the Bureau plans to study the effect of the handpiece on vibration in the near future.

Photographs of wave traces used to study vibration produced by dental instruments. A, Upper trace was produced by a standard frequency oscillator at 166 cps; lower trace by a diamond instrument 0.001 in. eccentric rotating at 10,000 rpm. Note low amplitude of 166-cy. component produced at this speed. B, Upper trace shows standard 166-cy. wave form; lower trace is large-amplitude, 166-cy. wave produced by a 0.007 in. eccentric diamond instrument, rotating at 10,000 rpm.









C, Trace was produced by an eight-bladed steel bur 0.001 in. eccentric, rotating at 10,000 rpm. The vibration frequency is about 1,300 cps. This is well above the frequency disturbing to most dental patients, and the low-frequency component is of very low amplitude. D, Trace shows the wave form produced by an eight-bladed steel bur 0.007 in. eccentric rotating at 10,000 rpm. The low-frequency component, 166 cps, is within the disturbing range and is of considerable amplitude.

In the course of the study on rotating dental instruments, the relative cutting ability of steel and carbide burs and of diamond abrasive wheels was compared. This was done by putting the bur or diamond wheel under investigation in the draw collet chuck and rotating it against an extracted human tooth. The tooth was held by a jig mounted on the roller carriage. It was pressed against the rotating instrument by means of suspended weights which were varied to produce different degrees of pressure.

The results showed that diamond instruments cut tooth enamel more rapidly at speeds of 10,000 than 5,000 rpm. Diamond wheels are many times more efficient than either steel or carbide when cutting tooth enamel. The cutting rates of both steel and carbide burs are similarly improved at the higher speed when cutting dentin. Carbide burs cut dentin at about twice the rate of steel burs at 10,000 rpm. In general, high speed rotation enables dental instruments to cut teeth faster with less pressure and with lessened probability of damage to tooth structure when proper cooling is employed. Many dentists feel that better control of the instrument results when high rotating speeds are used.

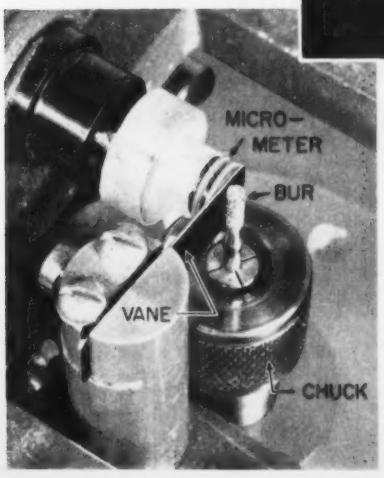
[1] *For further technical details, see* Factors influencing the cutting characteristics of rotating dental instruments, *by Donald C. Hudson, Jack L. Hartley, Robert Moore, and William T. Sweeney, J. Am. Dental Assoc.* **50,** *377 (1955).*

[2] *In a previous study the Air Force Dental Service and the Bureau showed that increased temperatures accompany high-speed rotation of dental instruments. For further technical details, see* Temperatures developed in rotating dental instruments, *by Donald C. Hudson and William T. Sweeney, J. Am. Dental Assoc.* **48,** *127 (1954).*

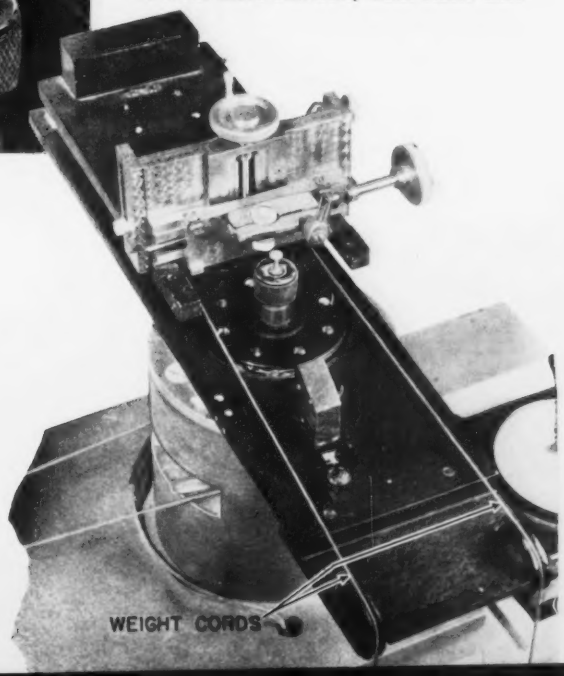
[3] H. F. vibration perception and frequencies, *by J. P. Walsh and H. F. Symmons, New Zealand Dental J.* **45,** *106 (1949).*

[4] *An earlier NBS development. See* Technical details of an electronic micrometer, *Electronics* **20,** *11 (Nov. 1947); also* Design criteria for mutual inductance transducers, *NBS Tech. News Bull.* **39** *(March 1955).*

Apparatus developed for vibration studies of rotating dental instruments. Steel vane bears against bur rotating in precision collet chuck. Movements of vane due to bur eccentricity are sensed by an electronic micrometer pickup. Pickup transmits vibration patterns to an oscilloscope whose screen shows vibrations as wave patterns that may be photographed and studied.



***Left* and *below*: Apparatus used to study the cutting efficiency of dental instruments. An extracted tooth is held by a jig mounted on the roller carriage. Pressure is adjusted by varying weights suspended from the cords. Steel, carbide, and diamond (shown here) instruments were rotated at speeds from 5,000 to 10,000 rpm. Results show that carbide burs cut dentin twice as fast as steel, but diamond instruments cut the hard enamel of teeth more efficiently than either bur.**



Low-Expansion Cobalt-Iron-Chromium Alloys

INFORMATION resulting from thermal expansion and phase transformation studies has confirmed [1] that the thermal expansion of certain cobalt-iron-chromium alloys is extremely low and nearly constant between 20° and 60°C. These findings of Peter Hidnert and Richard K. Kirby of the Bureau, who investigated a number of such alloys,[2] should be of interest to designers of equipment in which thermal expansion is important.

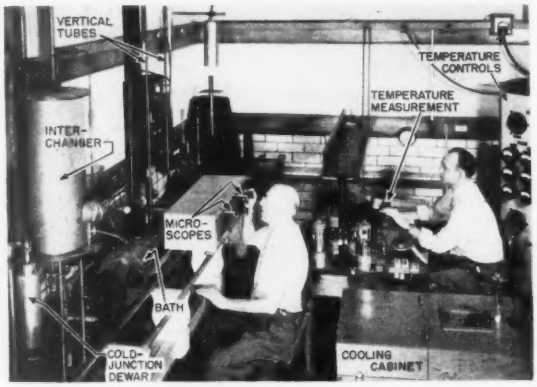
Scientists and engineers require low-expansion materials for applications in tools and machines, such as thermostatic and measuring devices, where some dimensional changes due to changes in temperature must be kept small. Generally fused quartz, invar, and some ceramics are used for such purposes. Of these, only invar is metallic, but it is subject to small but significant dimensional changes over long periods of time.

The Bureau's investigation indicates the existence of an alloy (36.6 percent of iron, 8.9 percent of chromium, and the balance cobalt) with a coefficient of expansion less than 1×10^{-6} per degree C for the range from 20° to 60°C. However, it was found that the low expansion of such alloys is very sensitive to small variations in their chemical composition. Also, some of them undergo a transformation on cooling at low temperatures.

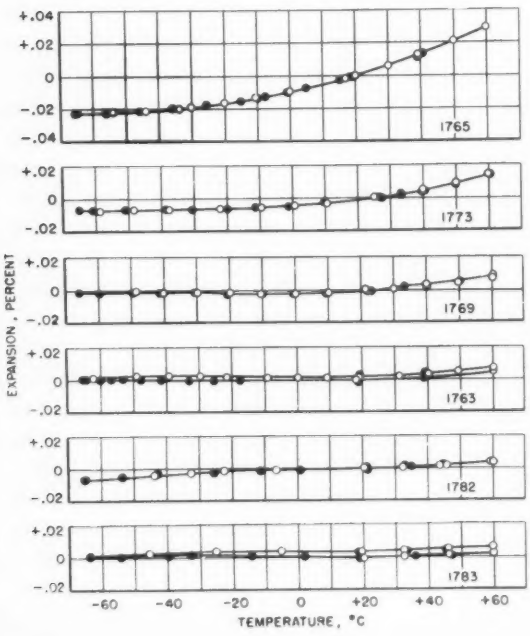
The experiments covered the temperature range from −196° to +1,000°C. Measurements were made on 19 samples, 30 cm in length, with iron contents varying from 36.2 to 37.2 percent and chromium contents varying from 8.6 to 9.9 percent by weight.[3] The linear thermal expansion of the alloys over the range from −65° to +800°C was determined with precision micrometric apparatus. Two microscopes mounted horizontally on a traveling comparator were used to measure the length changes in the sample as indicated by changes in the separation of two fine wires held in contact with the ends of the sample.

An electric furnace in which the sample is surrounded by air or an inert gas, was used to obtain temperatures between 20° and 800°C. A stirred-liquid bath was used for temperatures between −65° and +300°C; the temperatures below 20° were obtained by expanding compressed air from a liquid air interchanger through coils immersed in the bath.

The effects of various heat treatments from −196° to +1,000° C on the phase changes were studied with

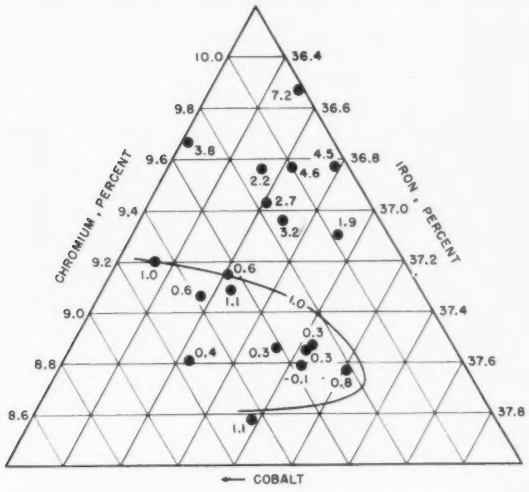


Apparatus used to measure the thermal expansion of low-expanding cobalt-iron-chromium alloys. Scientist at left is using micrometer microscopes to observe length changes in a sample rod. Rod is enclosed in a constant-temperature bath, shown in back of and slightly below the microscopes. Two fine wires, suspended through vertical tubes, are in contact with the sample's ends. Changes in separation of wires, as determined with microscopes, indicate changes in rod length. Temperature is measured and controlled electrically at right. Bath temperature was varied between —65° and +300° C. For measurements at higher temperatures, sample is placed in an electric furnace (not shown). The thermocouple cold-junction and liquid air interchanger for obtaining low temperatures in the stirred-liquid bath are at left. A cooling cabinet in right foreground contains additional low-temperature expansion apparatus.



Linear thermal expansion of six annealed cobalt-iron-chromium alloys. Some of these alloys whose chromium contents are between 9.1 and 9.9 percent have coefficients of expansion less than those for fused quartz and ordinary invar between −65° and +65° C. Points on heating curves are indicated by open circles, cooling curves by closed circles. The initial observation for each alloy (near 20° C) is plotted on the zero ordinate. Numbers in the lower right corners are laboratory numbers assigned to each sample as tested.

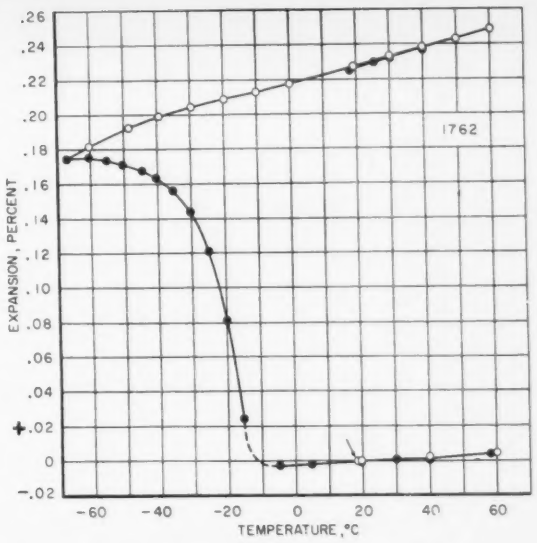
Ternary diagram indicates the close relationship between chemical composition and average expansion coefficient of low-expanding alloys in the range 20° to 60° C. Results disclose that low-expanding alloys lie within the elliptically shaped curve shown.



the aid of micrographs and by measuring the dimensional changes with micrometers and the expansion apparatus.

Of the samples investigated, those with chromium contents ranging from 8.6 to 9.2 percent have very low rates of expansion around room temperature. In fact, some of these alloys have coefficients of expansion less than those for fused quartz and ordinary invar between −65° and +60°C. However, on cooling to lower temperatures they undergo a first-order transformation of the martensitic type. This results in a low-temperature phase that has a very much higher rate of thermal expansion than the original high-temperature phase up to 200°C. The temperatures at which these transformations start were found to be as high as −10°C and decreased with increasing amounts of chromium content. The change in crystalline phase proceeds with discrete audible clicks and slight increases in temperature. A needle-like martensitic structure is finally produced. The reverse transformation, which reproduces the high-temperature phase, starts at about 600°C but is not complete until the material is heated above 900°C.

Further research is needed to develop additional information on the physical properties of these low-expanding alloys at various temperatures. In this way, the practicability of these alloys in commercial applications—such as the production of fine wire and surveying tape—can be determined.



Linear thermal expansion curve of a typical annealed cobalt-iron-chromium alloy (37.0 percent iron, 8.6 percent chromium). Coefficient of expansion is low in range from 0° to 60° C, but alloy is transformed to a low-temperature phase on cooling to −67° C. Expansion on cooling proceeds with discrete rapid increases in length, accompanied by audible clicks and slight increases in temperature. When sample is heated from −67° C, rate of expansion is found to be larger than it was for sample in its original annealed condition. Points on heating curves are indicated by open circles, on cooling curves by closed circles. An arrow indicates the initial observation.

[1] On the thermal expansion of alloys of cobalt, iron, and chromium, and a new alloy, "Stainless-Invar," *by H. Masumoto, Science Repts. Tôhoku Univ.* **23,** *265 (1934).*

[2] *For further technical details, see* Thermal expansion and phase transformations of low-expanding cobalt-iron-chromium alloys, *by Peter Hidnert and Richard K. Kirby, J. Research NBS* **55,** *29 (1955) RP2602.*

[3] *Samples were prepared for Eastman Kodak Co., Rochester, N. Y., by the Unexcelled Manufacturing Co., Cambridge, Mass. (now Unexcelled Chemical Corporation, Cranbury, N. J.).*

Symposium on Precision Gage Blocks

MORE than 90 scientists and engineers from the United States and abroad attended a Symposium on Precision Gage Blocks held at the Bureau in Washington, D. C. on August 11 and 12. Thirteen gage manufacturers were represented, as well as 10 gage using firms, 10 U. S. Government agencies, and 2 foreign government agencies. The sessions were largely devoted to the technical problems that underlie more precise measurement of industrial gage blocks.

In addition to discussion periods, 16 invited papers were presented by representatives of the Physikalisch-Technische Bundesanstalt, National Research Council

of Canada, E. I. DuPont de Nemours Co., Engis Equipment Co., C. E. Johansson Gage Co., Moore Special Tool Co., Sandia Corp., The Sheffield Corp., The Timken Roller Bearing Co., and the National Bureau of Standards. The program was arranged by I. H. Fullmer, Chief of the Bureau's Engineering Metrology Section.

Control of dimensions in modern mass production depends upon the accuracy with which gage blocks can be measured and used as reference standards of length. In recent years the increasing demands of industry for more precise measurement have made necessary higher-quality gage blocks and more precise, accurate, and convenient methods for measuring them. As a result, improved interferometers have been designed which use wavelengths of light as length standards in absolute measurement and intercomparison of gage blocks. Improvements have also been made in the sensitivity and accuracy of mechanical comparators, both those which are entirely mechanical and those which employ electrical transducers, amplifying circuits, and current meters as the means of measurement. Several gage measuring instruments of the different types, some developed commercially and others by or with the assistance of NBS, were exhibited in the Bureau's engineering metrology laboratories at one of the sessions.

The symposium provided an opportunity for those interested in more precise gage-block measurement to exchange ideas and to increase their understanding of the many problems encountered. A series of three papers dealt with the metallurgical and physical properties of gage block materials, with particular reference to dimensional stability. Another paper considered the characteristics of gage-block measuring surfaces, such as average roughness, depth of individual scratches, and condition of edges.

Six papers dealt with the application of interferometry to gage blocks, conditions affecting the accuracy of interferometric measurements, and the precision and accuracy attained in recent comparative length measurements by different laboratories. Two other papers were on recent improved interferometer designs.

The four concluding papers, as well as two formal discussions and an informal discussion period, were concerned with the development of commercial and government standards and specifications for gage blocks. Consideration was given to procedures for the surveillance of gage blocks after they have been in use.

Plans have been made for publishing all the symposium papers in a single volume.

Semimicro Dilution Viscometer

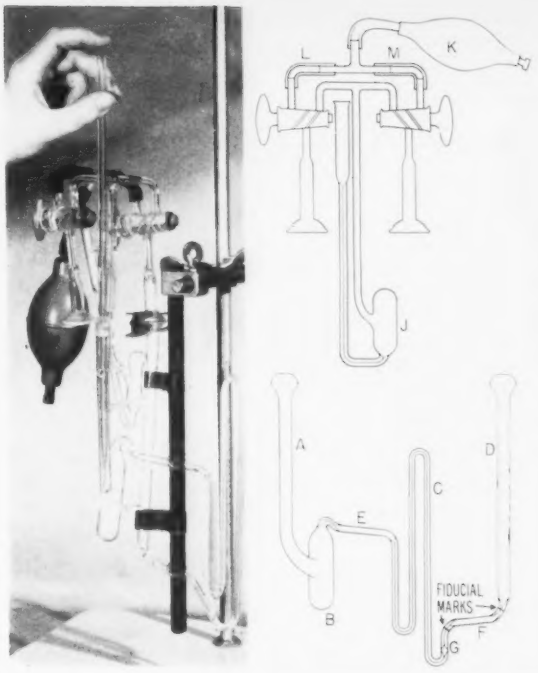
An accurate semimicro dilution viscometer developed recently promises to be of value in polymer research, where often only a small amount of polymer solution (approximately 1 ml) may be available for molecular weight determination. This instrument,[1] designed by Victor E. Hart of the polymer structure laboratory, differs from other semimicro viscometers in that it is suitable for dilutions and reruns of a solution. It also eliminates errors resulting from evaporation of the solvent.

In molecular weight studies of polymers, workers frequently need to determine viscosities of dilute solutions at several concentrations. This is facilitated by a viscometer that allows dilutions to be made by adding solvent directly to the solution in the instrument. However, the commonly used Ubbelohde dilution viscometer generally requires about 15 ml of solution. And when a viscometer design is reduced to semimicro scale, errors caused by drainage and surface tension effects usually increase. Although the Zeitfuchs cross-arm viscometer eliminates errors of this kind, it does not permit dilutions nor does it allow reruns to be made with the same liquid. The viscometer developed at the Bureau overcomes the disadvantages of both these instruments.

In the NBS viscometer, viscosity is measured in terms of the time required for a given quantity of the solution to flow through a triple-bend capillary. The device consists of two arms—vertical glass tubes about 6 in. long—connected by the capillary tubing system. A reservoir at the lower end of one arm contains the liquid to be studied. From the reservoir a nearly horizontal tube leads to the capillary which, in turn, leads to a similar, nearly horizontal tube that is directly below the first. The hydrostatic head between these tubes is the driving pressure that forces the liquid through the capillary. Fiducial marks at each end of the lower tube are used in timing the flow of liquid through the capillary. The viscometer is attached at the center of these tubes to a vertical, rubber-encased rod.

The two arms of the viscometer are topped by the male parts of spherical joints to which corresponding parts of a glass-valve assembly are attached. This assembly consists of a rubber suction bulb, a bubbler containing solvent, two 3-way stopcocks, and glass connecting tubing. By turning one of the stopcocks a half turn, the liquid in the viscometer can be drawn in the direction of the corresponding viscometer arm while air passes through the solvent in the bubbler and enters the opposite arm. The glass-valve assembly effectively eliminates evaporation losses from volatile solutions by: (1) providing a closed circuit for the vapor, in which there are no rubber parts, and (2) causing the air entering the instrument to become saturated with solvent in the bubler.

Before adding solution to the viscometer, the air within the instrument is first replaced with solvent-saturated air. This is done by operating the suction bulb to draw air through the solvent in the bubbler. The spherical-joint connection of the first arm is opened briefly, and the liquid inserted into the reservoir by means of a pipet. After inverting the viscometer in the proper direction, the liquid is drawn into the first horizontal tube until it begins to enter the capillary. The



Semimicro dilution viscometer for molecular weight studies of polymers. A solution for study is being introduced into the viscometer reservoir by means of a pipet. Rubber bulb at left is used in drawing liquid through the viscometer capillary. Viscometer gives accurate results with quantities of 1 ml, and usually no corrections are required.

Schematic diagrams of the semimicro dilution viscometer. *Top:* Glass valve assembly is attached to viscometer arms (A, D). Rubber parts (K, L, and M) are outside closed circuit provided for solvent-saturated air. By a half turn of one 3-way stopcock and use of rubber suction bulb (K), liquid can be drawn in direction of the corresponding viscometer arm. At the same time air passes through the solvent in the saturating bubbler (J). Position of stopcocks shown is proper while flow of liquid is being timed. Liquid is contained in reservoir (B). During run liquid flows through capillary (C) into tube (F). Driving pressure is hydrostatic head between (E) and (F). Fiducial marks for timing the flow are at each end of (F). Bits of liquid that remain in the capillary from a previous flow are collected into a uniform column with the main liquid body by bubble (G) blown in the capillary. In addition (G) serves as a convenient initial point to observe the meniscus. Because of the low surface tension of an organic solution, the tube (E) may be inclined slightly from horizontal to maintain a smaller upper meniscus during flow. Tube (F) is also inclined slightly from horizontal to facilitate drainage.

instrument is returned to the normal position and placed in a constant temperature bath. When the instrument and sample have attained bath temperature, the solution is drawn over the upper bend of the capillary until it continues to flow by gravity. After it passes the final fiducial mark, the liquid is drawn back into the reservoir. Between runs, more solvent may be added to the solution in the reservoir so that the viscosities of different concentrations of the solution can be determined.

The bends of the capillary and distances between them prevent siphoning over due to surface tension when the instrument is inverted for filling or reversed to working position. The capillary is long so that the diameter does not have to be too small (0.35 to 0.40 mm). Thus, erratic flow times due to dust or other particles in the capillary are seldom encountered. Because of the capillary length and the small volume of liquid, kinetic energy corrections are eliminated if the flow time is 100 sec or longer.

The viscometer has another advantage. The effects of shear rate in intrinsic viscosity determinations are negligible, even for very high molecular weight polymers in good solvents. Because of the design of the instrument, molecular weight determination should be practically free from all of the systematic errors found in viscometry.

The saturation bubbler in the glass valve assembly eliminates evaporation losses and is easier to operate than the rubber tubing arrangements of other viscometers. Rubber tubing has other disadvantages: it absorbs many solvent vapors and causes particles of rubber to clog the viscometer capillary.

In the study of thermally degraded polymers, for which the viscometer was designed, the instrument makes it practicable to obtain accurate data over wider extents of degradation than have previously been obtained. Such data are generally necessary as a basis for an adequate evaluation of the various theories that might explain the nature of the molecular weight changes. In addition, the viscometer should prove useful in other types of viscosity determinations. Although developed specifically for 1-ml quantities, its design is flexible so it may be constructed for larger or smaller volumes.

[1] *For further technical details, see* A semimicro dilution viscometer, *by Victor E. Hart, J. Polymer Sci.* **17**, *207 (1955).*

Publications of the National Bureau of Standards

Journal of Research of the National Bureau of Standards, volume **55**, No. 4, October 1955 (RP2617 to RP2625 incl.). Annual subscription $4.00.

Technical News Bulletin, volume **39**, No. 10, October 1955. 10 cents. Annual subscription $1.00.

Basic Radio Propagation Predictions for January 1956. Three months in advance. CRPL 134. Issued October 1955. 10 cents. Annual subscription $1.00.

Research Papers

Journal of Research, volume **55**, No. 4, October 1955. Single copies of the Journal vary in price. Single copies of Research Papers appearing in the Journal are not available for sale. The Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C., will reprint 100 or more copies of a Research Paper. Request for the purchase price should be mailed promptly to that office.

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SINCLAIR WEEKS, *Secretary*
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A. V. ASTIN, *Director*

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RP2617. Infrared absorption and emission spectra of carbon monoxide in the region from 4 to 6 microns. Earle K. Plyler, Lamdin R. Blaine, and Eugene D. Tidwell.

RP2618. Specific heats of collagen and leather. Joseph R. Kanagy.

RP2619. *p*H values of the Clark and Lubs buffer solutions at 25° C. Vincent E. Bower and Roger G. Bates.

RP2620. Heat capacity; heats of fusion, vaporization, and transition; and vapor pressure of N-dimethylaminodiborane, $(CH_3)_2NB_2H_5$. George T. Furukawa, Robert E. McCoskey, Martin L. Reilly, and Ann W. Harman.

RP2621. Phase equilibrium relations in the systems titania-niobia and zirconia-niobia. R. S. Roth and L. W. Coughanour.

RP2622. Synthesis of a fluoro talc and attempted synthesis of fluoro chrysotile and fluoro anthophyllite. Alvin Van Valkenburg, Jr.

RP2623. Determination of natural rubber in GR-S—natural rubber vulcanizates by infrared spectroscopy. Max Tryon, Emanuel Horowitz, and John Mandel.

RP2624. Thermal degradation of polychlorotrifluoroethylene, poly-α, β, β-trifluorostyrene, and poly-*p*-xylylene in a vacuum. S. L. Madorsky and S. Straus.

RP2625. Infrared transmittance of some calcium aluminate and germanate glasses. Jack M. Florence, Francis W. Glaze, and Mason H. Black.

Circulars

C557. Worldwide radio noise levels expected in the frequency band 10 kilocycles to 100 megacycles. W. Q. Crichlow, D. F. Smith, R. N. Morton, and W. R. Corliss. 30 cents.

C565. Techniques for ruling and etching precise scales in glass and their reproduction by photoetching with a new light-sensitive resist. Raymond Davis and Chester I. Pope. 30 cents.

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Low-capacitance power supply. J. H. Reaves. Radio-Electronic Eng. (64 E. Lake St., Chicago 1, Ill.) **24,** No. 5, 16 (May 1955).

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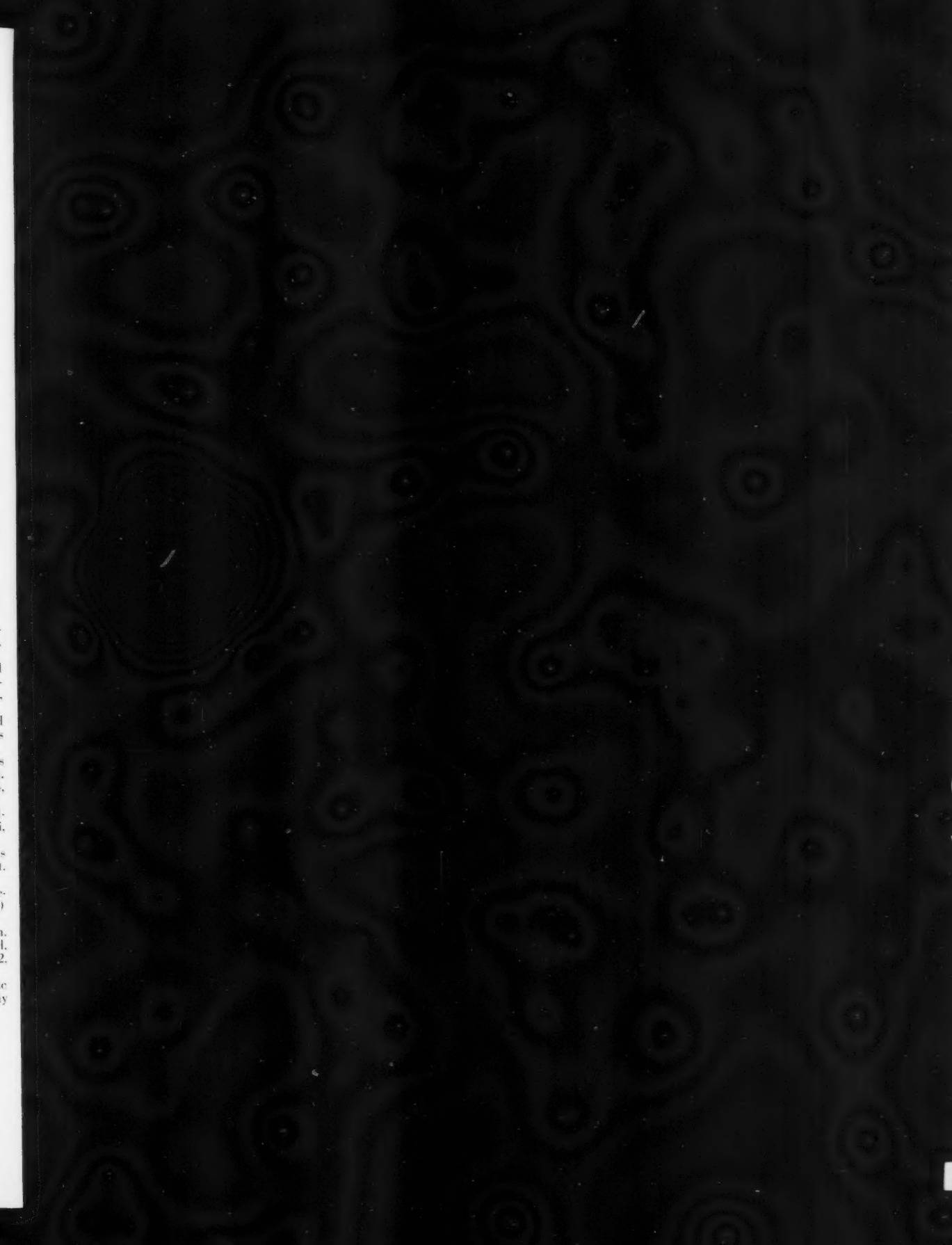
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